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Cone Calorimeter Evaluation of the Flammability of Composite Materials

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Abstract

A study was undertaken to evaluate the fire performance of composite materials
using the cone calorimeter as the bench-scale method of test simulating the
thermal irradiance from fires of various magnitudes. Five parameters were
derived from the calorimetry measurements to characterize the ignitability and
flammability of the composite materials.

Three of the parameters are, to a large extent, empirical since radiative heat
losses from the samples were unknown. These parameters are: 1) minimum
external radiant flux (MERF) required to produce pilot ignition in a
predetermined exposure time; 2) thermal sensitivity index (TSI) which
indicates the burning intensity dependence on external heat flux; and 3)
extinction sensitivity index (ESI) which indicates the propensity for
continued flaming combustion without an external heat flux. MERF values at
300 s for 3 mm composites panels of a FR epoxy resin and a poly(phenylene
sulfide) (PPS) resin composites were about 18 and 28 kW/m^2, respectively. The
TSI of the PPS resin composite had the greatest dependency on external flux.
Additionally, the ESI of the PPS composites was the only one to indicate an
external flux requirement to sustain combustion during the first 60 s after
ignition. The other two parameters determined were yields of gaseous products
of combustion and average extinction area, σ, normalized to the CO_2 yields.

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The values were found to be essentially constant at external fluxes ranging from 35 to 75 kW/m^2, with few exceptions.

1. Introduction

The purpose of this project is to assist the Navy with selection criteria for ship components made of synthetic resins or composites of fiber-reinforced resins by systematically assembling data on the flammability properties of these materials. The ultimate use of such a data base assembly is input for a method for accurately predicting the real fire performance and flammability characteristics of composites and resins from bench-scale tests. This is an interim report.

There are numerous naval ship components where the use of composites would provide substantial advantages over metals with respect to weight reduction, corrosion resistance, and design simplification. Furthermore, for some applications, the non-magnetic character of composites is uniquely advantageous. On the other hand, the resin matrix of a composite, being an organic component, presents an increased potential for fire hazard. Hence, in order to make wise engineering decisions assessing trade-offs, such as weight savings versus flammability, information must be available on the fire performance of candidate materials in various fire scenarios. A recent review [1]* found no report of bench-scale test methods by which the fire performance of materials could be predicted.

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*Number in brackets refer to references given at the end of this report.

The primary objective of this phase of the study is to determine the rate of heat release (RHR) of selected composites and resins burned under various levels of radiative heating. These levels simulate fire scenarios in which the composite material is itself burning or in which it may be near another burning material. The rate of heat release, $\dot{q}$, of fires, especially the peak $\dot{q}$, is the primary characteristic determining the size, growth, and suppression requirement of a fire environment [2]. This flammability characteristic can be measured using a bench-scale instrument. These values approximate the RHR of a surface element of a full-scale object in a real fire environment. Combined with other measurements, such as flame spread rate (the rate of growth of the surface element) and ease of ignition, the fire hazard contribution of the object can then in principle be calculated. Some such computational methods are already under development for other applications [3].

The calculations of Huggett [2] demonstrated that the average heat of combustion for a broad range of materials is a constant 13.1 kJ/g oxygen consumed, with an accuracy of ± 5% or better. Thus the RHR can be determined with good accuracy from two simple measurements, the flow rate of air through the combustion system and the oxygen depletion in this flow [4]. A bench-scale apparatus, the Cone Calorimeter, developed and described by Babrauskas [5], utilizes this oxygen consumption principle to determine the RHR per unit area $\dot{q}''$. The name "Cone Calorimeter" was adopted from the geometric configuration of its radiant heater. Data from this instrument can be used in research to predict the full-scale fire behavior of certain furnishings and wall lining materials [6]. The predictive method defines an environment as

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having n objects with surface areas divided conceptually into m small uniform areas, A, during combustion, so that q̇ at any time is given by

$$\dot{q} = \sum_{nm}(\dot{q}''_{n,m})(A_{n,m}) \tag{1}$$

The Cone Calorimeter has a well characterized and controlled irradiance source. Babrauskas and Parker [7] deduced that the spectral distribution of this source approximates the irradiance in compartment fires, where radiation is the primary process for energy transfer. Thus it was concluded that the instrument suitably determines the ignitability of upholstery and wood in fire-like environments.

We report the results of Cone Calorimetry measurements on a variety of composites and materials typical of those which may be used in ship components. The primary measurement using the Cone Calorimeter is RHR as a function of time under pre-selected, constant levels of irradiance simulating radiant fluxes from real fires of various magnitudes. Simultaneously-determined time-to-ignition, mass loss, combustion product yields, and smoke obscuration are also reported.

2.0 Materials

The materials used in this study are listed in Table 1. For the most part, only the generic classification of the resin and a general classification of the fiber reinforcement are known. Where greater detail of the materials is available, it will be indicated when the test results are presented. The generic classification of the resin and fiber identification were provided by the indicated sources. In general, the resin reinforcement was a glass fiber

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fabric except for a sample set of Ryton** panels in which carbon fibers were used. Several tests were performed on composite materials for which neither the identity of the fiber nor the resin was known. These latter tests were performed at the specific request of the Navy.

Test specimens were cut into 10 cm by 10 cm squares at the full thickness of the supplied product. The specimens were maintained at laboratory conditions (approximately 40-45% RH and 25°C) prior to testing.

3.0 Measurement Technique

The data reported here were obtained using the NBS Cone Calorimeter which is shown schematically in figure 1. The Cone Calorimeter and its function have been previously described by Babrauskas [5] and Babrauskas and Parker [7]. Briefly, it is a bench-scale rate of heat release calorimeter based on the principle of oxygen consumption [2]. The energy release rate is computed from the measurements of mass flow rate and oxygen depletion in the gas flow through the exhaust stack. An external radiant energy flux of up to 110 kW/m² may be applied to the surface of a sample by a temperature-controlled radiant cone heater. An electric spark igniter mounted above the specimen was used to ignite the pyrolysis products generated by a specimen exposed to a preset irradiance. The ignition delay time for each composite material usually was

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**Certain commercial materials are identified in this report in order to adequately specify the experimental procedure. In no case does such identification imply recommendation by the National Bureau of Standards nor does it imply that the material identified is necessarily the best available for the purpose.

measured at three different radiant flux levels. In general, specimens are exposed to flux levels of 35, 50, and 75 kW/m^2. Ignition delay time measurements were made by an operator with a stop watch as part of the standard test procedure used to determine the rate of heat release. Samples were placed under the cone heater and the amount of time necessary to ignite the evolving decomposition products by the spark of an electric arc was recorded.

A load cell was used to continuously measure changes in sample mass, while products of decomposition, (i.e., CO, CO_2, and total unburned hydrocarbons) were monitored by appropriate gas analyzers. By combining the mass loss data and the gas concentration data, specific gas species yields were computed (mass of product/unit mass of material gasified). Smoke obscuration was characterized by the attenuation of a laser beam and reported as the extinction area per unit mass of material consumed. Data from all the measurement devices were collected every five seconds by a digital data acquisition system and stored for later data reduction.

4.0 Results and Discussion

4.1 Ignition

The objective here is to obtain a measure of the resistance of materials to pilot ignition under radiative heating. The number of different radiant flux levels and the replication number were limited by material availability.

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Therefore, for example, the Koppers Dion sample was tested in duplicate at four flux levels (the three cited above plus 25 kW/m^2), while ignition of the Corflex assembly was measured at only three flux levels.

The times to pilot ignition are reported in Table 2. Where duplicate measurements were made, the average values are reported (one half of the difference between the two measurements is shown in parentheses). As expected, the data show that as the incident flux increases the ignition delay time decreases. It should also be noted that the range of ignition delay time for all materials tested at a given radiant flux increased with decreasing radiant flux (figure 2), with ranges of 21 s to 55 s at 75 kW/m^2 and 92 s to 390 s at 35 kW/m^2. Therefore, in very large fires, one might expect similar ignition-delay times for all composites, whereas in incipient fires one would expect ignition-delay times to depend on the chemical composition of the resin and configuration of the material.

There are two possible modes of radiative ignition: one is auto-ignition and the other is pilot ignition. Auto-ignition results solely from the external heating of the material substrate, without the presence of a high temperature source near the material surface. Pilot ignition refers to forced ignition of the fuel vapors by a high temperature pilot source such as a hot wire, spark, or small flame. For auto-ignition to occur, the fuel/air ratio above the material substrate must be within the flammability limits and the gas phase temperature must be above an ignition temperature. Because of the existence of an intentionally supplied hot spot, pilot ignition only requires that the

fuel/air ratio above the material substrate in the vicinity of the pilot
source be within the flammability limit.

The gasification (pyrolysis) rate of the resin controls the speed at which the
vapor concentration at the composite surface approaches its lower flammability
limit. The gasification rate is temperature dependent. Therefore, it appears
reasonable to suppose that ignition occurs only after the surface temperature
of the resin has reached a critical level, the ignition temperature. This
ignition temperature could vary somewhat with ignition conditions, such as
heat flux level, on char-forming materials due to the insulating effect of the
char.

Kashiwagi [8,9] investigated the effect of external radiant flux on the
surface temperature at ignition and the ignition delay time of red oak and
poly(methyl methacrylate) (PMMA) in auto- and pilot-ignition modes. He used a
high powered CO_2 laser to irradiate (60-160 kW/m^2) the sample surface, while
simultaneously measuring sample surface temperature with a small diameter
chromel-alumel thermocouple. An electrically heated wire was placed near the
sample surface for pilot-ignition tests. These tests showed
that for PMMA the surface temperature of the substrate at ignition was
relatively constant, approximately 400°C, for both auto- and pilot-ignition
modes. The surface temperature of red oak, a char former, at ignition
increased as the external flux decreased.

Atreya [10] reported results of tests on different types of wood and found
that, for the pilot-ignition mode below an external flux of 25 kW/m^2, the wood

surface temperature at ignition increased with decreasing external radiant flux. Above 25 kW/m^2 the surface temperature at ignition was constant at approximately 350°C.

Rasbash et al. [11] used an electrically heated radiant panel to irradiate samples of PMMA at 11 kW/m^2 and above. Using a small hydrogen flame as a pilot, they found that surface temperatures decreased slightly with decreasing external radiant flux. At 24 kW/m^2, the reported surface temperature was about 275°C and decreased to 250°C at 11 kW/m^2. This is about 150°C below the value reported by Kashiwagi [9]. Instrument-dependent conditions for surface temperature measurement may account for the differences in pilot-ignition results between Kashiwagi and Rasbash.

Thomson and Drysdale [12] measured the surface temperature at ignition in the presence of a pilot flame of six common thermoplastics using two different instruments over an irradiance range of 10 kW/m^2 to 40 kW/m^2. Table 3 summarizes their results. Within experimental error, they found that the surface temperature at ignition was not significantly affected by changes in the level of external radiant flux, above some minimum value. This is indicative of a unique ignition temperature for a range of irradiance levels. These thermoplastic materials are known to undergo gasification by pyrolysis without significant secondary reactions such as char formation reactions. Simple bond scission of aliphatic carbon chains will lead to volatile and combustible products.

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Brown [13] recorded the surface temperature of a series of composite panels exposed to different radiant flux levels in the cone calorimeter. Table 4 summarizes those results for the surface temperature at pilot ignition using an electric spark. While the data show some scatter, in general, the surface temperature at ignition is relatively constant for each material and is greater than the thermoplastics above (Table 3) due to enhanced stability from cross links and aromatic components.

All of the materials listed in Tables 3 and 4 behave qualitatively the same as those shown in figure 2 with respect to ignition and radiant flux. The presence of inorganic fibers does not appear to alter the ignition behavior. If it is then assumed that this trend is applicable in general to all composites (i.e. that the pilot ignition occurs at a fixed surface temperature, dependent only on the thermal gasification characteristics of the substrate), one can use the simple thermal heat-up model derived by Carslaw and Jaeger [14] to suggest a form or trial function that ignition-delay time might have with respect to the heat absorbed from the constant external radiant flux. Heat losses are ignored in this simple model. Furthermore, this model assumes that the substrate can be treated as an inert, thermally thick, and opaque solid. Then the delay time to reach the ignition temperature is given by:

$$ t_{ig} = \frac{\pi k \rho c}{4} \left(\frac{T_{ig} - T_o}{\dot{q}} \right)^2 \qquad\qquad (2) $$

where

t_{ig} = ignition delay time (s)
k = thermal conductivity (kW/m/K)
ρ = density kg/m^3)

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c     = heat capacity (kJ/kg/K)
T_ig  = ignition temperature (K)
T_o   = initial temperature (K)
q̇     = external radiant flux absorbed at the surface of the solid (kW/m²)
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Equation (2) shows that the ignition delay time, t_{ig}, is proportional to $1/\dot{q}^2$

provided, however, that the temperature wave does not reach the back surface

of the sample before ignition. If, however, the material is thermally thin,

that is, if the thermal wave hits the back surface before ignition occurs, the

solid material will have an ignition delay proportional to about $1/\dot{q}$.

Additionally, equation 2 provides an approximate basis for determining the

influence of k, ρ, and c on ignition behavior. Therefore, a log-log plot of

ignition time versus flux should give a straight line with a slope of minus 2

for an inert, thermally thick, and opaque material. Figure 3 shows the

results for the Koppers Dion 6692T panel 25 mm thick and a Corflex panel, 3 mm

thick. A linear regression line drawn through these data results in negative

slopes for the two lines of 2.3 and 1.7, respectively, for the Koppers and

Corflex panels. Table 5 is a listing of the slope of the regression line for

each composite. It is recognized that derived values are essentially

empirically based since heat losses are not known. However, plots of the data

appear to be linear as was shown by typical examples in figure 5. Moreover,

ignition apparently occurs before the thermal wave penetrates the back

surface.

Plotting ignition-delay data for all Cone Calorimeter experiments (Table 2) as

illustrated in figure 3 allows one to extrapolate the regression line to some

chosen location. Extrapolation to 600 s, the recommended time limit for

ignition in this apparatus, represents the minimum external flux (MERF)

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necessary to produce pilot ignition after a protracted exposure of 600 s to irradiative heating. The MERF values (at 600 s) are listed in table 5, although these values may not be completely realistic because of the extensive extrapolation (for some materials) from a limited data range. Moreover, a real fire on a ship, whose radiant flux requires at least 600 s for pilot ignition of a composite material, is expected to be detected and suppressed before the composite becomes involved in the fire growth. A more practical application of the ignition times would involve determining the required irradiance to cause ignition at some other time, such as 300 s, for example. This represents an estimate of the maximum external flux from a fire in the environment where composites are used that the composite could withstand before the material would begin to contribute to the fire growth. The values obtained at 300 s are also listed in Table 5 and are called $MERF_{300}$. Although the data for ignition are very limited, the maximum deviation of the regression slope from the theoretical value of minus 2 towards a value of minus 1, was 0.5 (25%) for the 3 mm Derakane panel. This difference, in part, may be due to heat loss from the back surface of the thin sample. Similar effects may be attributed to the thin Corflex panel even though the regression slope, minus 1.9, closely approximates the idealized value, minus 2. These materials indicate the lowest MERF values for ignition 12 and 18 kW/m^2, respectively, for $MERF_{600}$ and $MERF_{300}$.

4.2 Rate of Heat Release

We present in this section the Cone Calorimeter results on the heat released as measured by the oxygen consumption during the combustion of several

materials under radiative heating in a fully ventilated atmosphere (21% oxygen). It has been established [2] that the carbon in organic materials need not be fully oxidized to carbon dioxide for the relationship of 13.1 kJ of heat released per gram of oxygen consumed to hold true. Thus, typical reaction products of combustion in fire environments, consisting of partially oxidized pyrolysis products, such as, hydroxy and carbonyl compounds and soot, do not significantly affect the accuracy of the Cone Calorimeter results.

Results of heat release rates were obtained here for a broad range of resins, including epoxy, polyester and poly(aryl thio-ether) resins, whose structures and chemical compositions are very different, suggesting individual degrees of susceptibility to oxidation and gasification under radiative heating.

Profiles of the rates of heat release with respect to time, under constant external irradiance, were found to have features which are unique to the composite studied. The profiles appear to depend primarily on the chemical composition of the resin and the thickness of the composites. Figures 4, 5, and 6 demonstrate typical variations observed in the RHR-time profiles of, respectively, a 25 mm (1 inch) thick polyester/glass fiber (Koppers Dion 6692T), a 3 mm (1/8 inch) thick epoxy/glass fiber panel (Corflex), and a 3 mm thick poly(phenylene sulfide)/glass fiber (Ryton) composite panel, each of which was radiatively heated at 35, 50, and 75 kW/m^2. The polyester composite also was radiated at 25 kW/m^2. In each of the figures, the curves for the composite generally show an initial sharp rise in the RHR which occurs at about the time of ignition and increases to a maximum or peak RHR for each irradiance level. The peak RHR duration is short. The subsequent decrease in

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irradiance level. The peak RHR duration is short. The subsequent decrease in initial RHR is attributed to increase in thickness of the char layer. The char layer reduces the transfer of heat to the substrate (resin) below the surface thereby reducing the rate of gasification of the resin.

In general, all of the curves exhibit at least two maxima for RHR. The initial peak is due to surface volatilization and char formation, as discussed above. The second peak is a result of an increase in the gasification rate of the unburned substrate (mass loss rate data will be discussed below) caused by an increase in the bulk temperature of the substrate. The bulk temperature increases because the unburned substrate is no longer thermally thick, i.e., the thermal wave has reached the back surface. Back surface temperatures should increase as the second peak of RHR is approached. While these measurements were not made in this investigation, Parker [15] has shown the same phenomenon with wood, a char forming material. He observed two maxima in RHR; the second peak increased as the back surface temperature increased.

The separation with respect to time of the RHR maxima is dependent on the sample thickness, irradiance level and chemical composition of resin. For example, the 3 mm thick Corflex and Ryton panels tested at 35 kW/m^2 have peak separation times of about 150 s and 350 s, respectively. This difference is attributed to the chemical composition of the resins, the difference in thermal properties, and difference in flame heat feedback rates.

It may be seen that the intensity of the RHR follows the rate at which volatiles are pyrolyzed from the specimens, and, to a large extent, is

indicative of the thermal stability of the resin and its propensity to gasify. The mass loss rates with respect to time of the polyester, epoxy, and PPS composites are shown, respectively, in figures 7, 8, and 9. The purpose of presenting the mass loss curves at this time is to show that the dq''/dt versus time curves follow the time profile of mass loss rate, dm''/dt, versus time curves. The ratio of these two quantities ($\dot{q}''/\dot{m}''$) at any given time is the effective heat of combustion ($\Delta h_{c,eff}$) of the gases evolved at that time. The mass loss rates and heat of combustion will be discussed further in a later section.

Since the RHR, in most cases, changes quite significantly with time, it appears that more meaningful information may be gained about the fire behavior of the composites under radiative heating if the rates of heat release are averaged over periods of time during the burning process. Not only are the advantages of curve smoothing brought forward to clarify trends in the heat release data, but Babrauskas and Krasny [16] demonstrated that the rate of heat release averaged over 180 s could best be used to predict the fire performance of upholstered furnishings in large-scale experiments. Kanury and Martin [17] also have used average values for deducing physicochemical properties of essentially homogeneous materials in fire environments. The proposed ASTM Method P 190 [18] specifies that average $\dot{q}''$ values for the first 60, 180, and 300 s after ignition, or for other appropriate periods, be included in the report of the cone calorimeter results. In addition to the recommended practice in ASTM P 190, the average RHR over 60 s intervals from ignition are reported.

Figure 10a shows a plot of the RHR averaged as recommended in P 190 from
ignition up to 360 seconds for the Koppers composite under the four irradiance
levels previously mentioned. A similar plot, figure 10b, shows the 60 s
interval averages for the RHR. As expected, the recommended procedure shows a
rather smooth change in the average RHR up to 360 s after ignition. In every
case this includes the initial peak RHR's but may not include the second
maximum. The effect of irregular volatilization of fuel from the surface is
reduced. Figure 11b shows a more irregular pattern. However, the first 60 s
intervals are identical. Figures 11a/11b are similar plots for the Corflex
composite which shows more distinction between the irradiance levels for the
first two minutes. Thereafter, the curves tend to coalesce or merge around
180 seconds after ignition as the effect of the back surface is felt.
Figures 12a/12b demonstrate the behavior of the average RHR of Ryton composite
over the post-ignition period. This composite shows, as previously suggested,
the greatest sensitivity to irradiance level. The lowest irradiance level, 35
kW/m^2, as was seen in the ignition data, provides barely enough energy to
promote combustion. On the other hand, the average RHR at irradiances of 50
and 75 kW/m^2 provides for an increasing average until 300 and 240 s,
respectively, when the panels are burned out.

The cone calorimeter results obtained in this study on the rates of heat
release averaged at the various times, as previously indicated, are presented
in tables 6 through 13. Table 6 presents all of the results obtained for the
25 mm thick Koppers polyester composite. This table includes the data
illustrated in figure 10. The $\dot{q}''$ value averaged at 60 s for one of the

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specimens tested at 35 kW/m^2 appears to be larger than expected. An explanation for this behavior is not known at this time.

Table 7 summarizes average RHR, $\overline{\dot{q}}''(t)$, values for a 13 mm (1/2 in) thick Koppers polyester composite consisting of various configurations of glass fiber reinforcements in composites containing 42% and 54% of brominated (fire retardant) polyester resin and in composites containing 42, 43, and 51% of the non-brominated polyester matrices. The glass fiber reinforcements in the composites include (1) fibers woven into a mat from continuous strands and then stitched along with other chopped fibers (stitched woven roving and chopped strand); (2) reinforcements from woven roving and woven mat; and (3) non-woven spirally interlocked fiber mat. The effect of bromine as a flame retardant can be seen readily by comparing the average $\dot{q}''$ values at 60 s of the untreated samples (first three samples listed) with the two bromine containing samples. It appears that the presence of bromine in the polyester results in a reduction of average $\dot{q}''$ on the order of 35 to 40% overall. On the other hand, we note that the average $\dot{q}''$ values of the brominated specimens in this table (which were 13 mm thick) are generally a factor of two greater than the average $\dot{q}''$ of the 25 mm specimens radiatively heated at 50 kW/m^2 shown in table 6. The difference in any rate of heat release may be attributed, in part, to the difference in sample thicknesses, i.e., 25 mm versus 13 mm, but other unknown factors are also responsible for the early differences. The thicker samples provide a greater heat sink resulting in a smaller volume of resin being raised to the decomposition temperature per area of surface irradiated. This trend is also seen in T_{ig} at about 40 s for the 13 mm sample and T_{ig} of about 60 s for the 25 mm sample (Table 2).

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Next, the average q̇" values are summarized for three types of epoxy resin composites. The average q̇" values of a fire retardant epoxy are listed in Table 8. Tests were performed on the assembly as received and on the individual outer panels. These results show that there are only small differences between the average RHR values of the thermally thin (3 mm) and thick assemblies (about 37 mm) and suggest that the heat loss from the back surfaces of the thin samples is relatively small as a result of effective insulation in the sample holder. The results for the composite with a vinyl ester type of epoxy resin are listed in Table 9. The average q̇" results for the third resin type, high performance epoxy resin composite prepared at DTRC laboratory [13], are shown in Table 10. Although the composition of the resin is not known beyond it being an amine-cured epoxy resin, it appears that the fire performance of this latter resin closely resembles that of the FR epoxy composite shown in Table 8.

Table 11 summarizes the average RHR of the four Ryton (PPS) panels. We note that ignition did not occur when specimens reinforced with woven carbon fibers were heated at a flux of 35 kW/m^2. The same result was found for one specimen reinforced by a swirl mat of glass fibers. Overall, the RHR at this flux level is low. Where results are not reported at the various post-ignition times, sustained flaming combustion did not occur. The average q̇" results of another composite prepared at DTRC from a bismaleimide (BMI) and graphite fibers and tested at NBS are listed in Table 12 [13]. The results from an experimental composite, prepared from vinyl styryl pyridine and BMI, and reinforced with glass fibers are shown in Table 13. This experimental

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composite which is designed as a heat shield, is composed of only two plies of fibers ($\simeq$ 1 mm). Having such a low mass per unit surface area contributes to low rates of heat release and fairly short periods of flaming combustion. It may be seen in reviewing the average $\dot{q}"$ data in Tables 6 through 13 that the composites with polyester and epoxy resins generally show maximum $\dot{q}"(t)$ values in the first 60 s post ignition. The $\dot{q}"(t)$ values generally decrease with time after the first 60 s which suggest that the peak RHR is associated with initial surface burning of the composite rather than subsequent combustion of the pyrolyzate from the interior of the composite. For irradiances of 50 kW/m^2 or more, the composites with PPS, BMI, and vinyl poly(styryl pyridine)BMI resins show maxima at times greater than 60 s. For these samples, the maximum $\dot{q}"(t)$ is not the initial peak.

4.3 Fire Sensitivity Indices

Kanury and Martin [17] and Kanury [19] reported simplified models by which heat release rates (peak, instantaneous, and average values) may be related to basic properties of materials in fire environments using the Spalding B number concept. These authors and Tewarson and Pion [19] deduced from energy conservation at the sample surface that the heat release rate $\dot{q}"$ may be expressed by the following equation

$$\dot{q}" = (\Delta H_{c,eff}/L)[\dot{q}"_T + \dot{q}"_e - \dot{q}"_\ell] \tag{3}$$

where

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$\Delta H_{c,eff}$ =   effective heat of combustion

L =   heat of gasification (pyrolysis)

$\dot{q}_T''$ =   heat transferred from flame to material surface

$\dot{q}_e''$ =   imposed external flux

$\dot{q}_\ell''$ =   heat flux loss by the surface to ambient

The slope ($\Delta H_{c,ff}/L$) of a plot of the measured RHR against the external radiant flux provides one measure of the flammability of materials; it is a key determinant of the B number value. This parameter, the thermal sensitivity index (TSI) [17], provides a basis by which the fire performance of the materials may be indexed and compared over a broad range of external irradiances, simulating different fire environments. The intercept of such a plot in principle indicates whether the flame is self-sustaining in the absence of an external irradiant flux for the time period under consideration. We will call this parameter the extinction sensitivity index (ESI); Kanury and Martin [17] called this parameter the limiting thermal index. Equation 3 can be expressed as

$$\dot{q}'' = (TSI) \cdot \dot{q}_e'' + (ESI). \tag{4}$$

We illustrate the dependence that the average RHR has with respect to imposed heat flux levels by plotting the average $\dot{q}''$ at 60 s versus external flux, $\dot{q}_e''$. Using 60 s average $\dot{q}''$ minimizes the effect of sample thickness and conductive heat losses. Figure 13 show the results for composites whose resins are polyester, FR epoxy, poly(phenylene sulfide), and BMI. This plot illustrates the TSI and ESI at 60 s interval on resin composition.

Table 14 summarizes the slopes, intercept, average effective heat of combustion, and minimum external radiant flux ($MERF_{300}$) necessary for ignition within 300 s. The ESI values (slopes) are estimates of the sensitivity of the combustion intensity to variations in external irradiance and show that the Koppers composite, Corflex Panel Assembly, and BMI Panel had about the same sensitivity to variations in $\dot{q}_e$". Because of differences in sample thickness these samples should not be compared to each other without caution. However, the TSI values indicate that the rate of heat release of these samples, although not the same in magnitude, would be fairly insensitive to small changes in external irradiance. This suggests that in a real fire the decay in an external fire imposing energy on a target material made from one of these composites would not be reflected as rapidly in a reduced heat release rate of the target material as compared to the materials with higher TSI values. For example, the Ryton Panels, which ranged in value from 1.3 to 1.8, would be expected to respond most strongly to variations in source irradiance.

The Ryton Panels also exhibited a negative intercept, ESI. This suggests that the heat loss from the flame is greater than its flux to the surface. With the removal of an external heat source these materials can be expected to self-extinguish, while the other materials with a positive ESI would be expected to continue burning at least for the first 60 s. The intercepts indicate that the epoxy matrix composites exhibit the most potential for sustained combustion with an external radiant flux following ignition.

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In Table 14, the effective heat of combustion values are averages taken from each exposure over the entire measurement; they are computed from the ratio of $\dot{q}''$ to mass loss rate, $\dot{m}''$. These values fall into two groups, the lower one (about 12 kJ/g) where the resin is flame retarded and the upper values (20-25 kJ/g) where it is unretarded.

The minimum external radiant flux ($MERF_{300}$) values necessary for ignition within 300 s are repeated here for comparative purposes; ignitability is another important flammability parameter that does not depend on the same fuel characteristics as rate of heat release.

4.4 Product Generation

Table 15 summarizes the combustion product yields and mass loss at the various radiant flux levels. Average values obtained from entire experimental periods are reported since the quantities generated remained fairly constant with time (see figures 18 and 19 for CO and CO_2, respectively). The values for hydrocarbons (HC), CO, and CO_2 yields have been normalized to the sample weight loss. While all of these tests were conducted under well-ventilated conditions, combustion efficiency can still be determined by the CO/CO_2 ratio and the HC/CO_2 ratio, Table 16. The data indicates that, in general, the CO/CO_2 ratio is independent of external irradiance, with the exception of Ryton Swirl Mat Panel. For this panel the CO/CO_2 ratio decreases with increasing irradiance. The Koppers composites show a flux dependence on the HC/CO_2 ratio such that it decreases with increasing flux, while the other materials are constant with flux variations.

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Smoke obscuration reported here is the average specific extinction area, σ(avg), given by

$$\sigma(\text{avg}) = [(\Sigma_i \dot{V}_i \Delta t)/(m_i - m_f)]\ [(1/L)\ln(I_o/I)] \qquad (5)$$

where

$\dot{V}$	=	flow rate in exhaust duct (m^3/s)
Δt	=	time interval of measurement(s)
$m_i - m_f$	=	mass loss (kg)
L	=	distance through which light is measured (m)
I_o	=	initial light intensity
I	=	final light intensity

In Table 16 are listed the σ/CO_2 ratios for the materials tabulated in Table 15. In general, the σ/CO_2 ratio is constant for a material over the range of irradiances investigated. However, as with the HC/CO_2 ratio, the σ/CO_2 ratio for the Koppers composite show a similar apparent dependence on external irradiance. Also the σ/CO_2 ratio for the lab epoxy, BMI, and Ryton Swirl Mat are an order of magnitude less than the Corflex Panel and nearly two orders of magnitude less than Koppers. This indicates that one of these three materials would be best suited for applications where smoke obscuration is a primary concern.

5.0 Summary of Results

The cone calorimeter was used to evaluate the fire characteristics of a series of composite materials. Ignition delay time, heat release rate, yield of gaseous products and smoke were measured.

The results of an analysis of the ignition delay time data showed that:

- $T_{ig} \propto 1/\dot{q}^2$ was a usable, but simplified approximation of the data; one must be cautious in extrapolating the data with it.

- This relationship applied to all of the composite materials including the sandwich assembly (i.e. Corflex).

- There is some indication that the slope of the regression line, for a given material composition is a function of the thickness of the material (e.g. Derakane Panels and Corflex Assembly versus Corflex Panel).

- Given the limited data set, glass fiber configuration appear to have no effect on ignition delay time.

The results of an analysis of heat release rate data show that:

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- Thermal sensitivity index (TSI) and extinction sensitivity index (ESI) can be inferred from the external heat flux dependence of the average rate of heat release during the first 60 s after ignition.

- The TSI and ESI values were inferred from averaged RHR data related to the external flux by regression analysis as defined to show:

$$\dot{q}'' = TSI \cdot \dot{q}_e'' + ESI$$

- TSI values indicate a dependence of fire growth rate on external flux during combustion.

- ESI values indicate whether a composite is expected to self-extinguish during the first 60 s of combustion if the external heat flux is removed.

- Comparison of the TSI or the ESI values to MERF values show no correlation.

Product generation data show that the HC/CO_2, CO/CO_2, and σ/CO_2 ratios were essentially constant with external irradiance (from 35 kW/m^2 to 75 kW/m^2) for the various composites tested. However, three exceptions were found:

- a FR polyester and a FR epoxy resin composites showed a decreasing HC/CO_2 ratio with increasing external irradiance;

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- the PPS composite showed a decrease in CO/CO_2 ratio with increasing external irradiance; and

- the PPS and BMI resin composites σ/CO_2 values were an order of magnitude less than the epoxy and polyester resin composites.

6.0 Conclusions and Recommendations

The Cone Calorimeter can measure an array of flammability parameters for composite materials. These include the external radiant flux requirements for pilot ignition and sustained flaming combustion, the flux dependency of the rate of heat release, and the relationship of flux level to combustion efficiency as reflected in the yields of combustion and pyrolysis products. Since these measurements are based in the fundamentals of fire science, we expect they will correlate well with the larger-scale compartment fire behavior.

Thus, this development represents the first step towards predicting the performance of composite materials in various fire environments. Therefore, we recommend investigating the use of these parameters from the Cone Calorimeter and, additionally, a radiant-flux-based flame spread index to provide the basic data from bench-scale measurements for correlation with larger-scale (quarter scale and full scale, for example) compartment fire measurements. The bench-scale parameters will then serve as input for hazard prediction models of the type already under development at the NBS Center for Fire Research.

Acknowledgments

References

[1]   Brown, J.E., Loftus, J.J., and Dipert, R.A., "Fire Characteristics of
       Composite Materials: A Review of the Literature", NBSIR 85-3226, U.S.
       Dept. of Commerce, National Bureau of Standards, Gaithersburg, MD 20899.

[2]   Huggett, C., "Estimation of Rate of Heat Release by Means of Oxygen
       Consumption Measurements", Fire and Materials, $\underline{4}$, 61 (1980).

[3]   Bukowski, R.W., Jones, W.W., Levin, B.M. Forney, C.L., Stiefel, S.W.,
       Babrauskas, V., Braun, E., and Fowell, A.J., "Hazard I. Volume 1: Fire
       Hazard Assessment Method", NBSIR 87-3602, U.S. Dept. of Commerce,
       National Bureau of Standards (1987).

[4]   Parker, W.J., "Calculation of Heat Release by Oxygen Consumption for
       Various Applications", J. Fire Sci. $\underline{2}$, 380 (1984).

[5]   Babrauskas, V., "Development of the Cone Calorimeter - A Bench-Scale
       Heat Release Apparatus Based on Oxygen Consumption", Ibid $\underline{8}$, 81 (1984).

[6]   Babrauskas, V., "Bench-Scale Methods for Prediction of Full-Scale Fire
       Behavior of Furnishings and Wall Linings", Technology Report 84-10,
       Society of Fire Protection Engineers, Boston, MA.

[7]   Babrauskas, V. and Parker, W.J., "Ignitability Measurements with the
       Cone Calorimeter", NBSIR 86-3445, U.S. Dept. of Commerce, National
       Bureau of Standards (1986).

[8]   Kashiwagi, T., "Experimental Observation of Radiative Ignition
       Mechanisms", Combustion and Flame, $\underline{34}$, 231-244 (1979).

[9]   Kashiwagi, T., "Effects of Sample Orientation on Radiative Ignition",
       Combustion and Flame, $\underline{44}$, 223-245 (1982).

[10] Atreya, A., "Pyrolysis, Ignition and Fire Spread on Horizontal Surfaces
       of Wood", NBS-GCR-83-449, U.S. Dept of Commerce, National Bureau of
       Standards (1984).

[11] Rasbash, D.J., Drysdale, D.D., and Deepak, D., "Critical Heat and Mass
       Transfer at Pilot Ignition and Extinction of a Material", Fire Safety
       Journal, $\underline{10}$, 1-10 (1986).

[12] Thomson, H.E. and Drysdale, D.D., "Piloted Ignition of Plastics",
       Proceedings of Fundamental Aspects of Polymer Flammability, Eds: Cox, G.
       and Stevens, G., Institute of Physics Short Meetings Series #4, London,
       England (1987).

[13] Brown, J.E., "Report of Test on Combustion Characteristics of Fiber
       Reinforced Resin Panels", FR-3970, U.S. Dept. of Commerce, National
       Bureau of Standards (1987).

[14] Carslaw, H.S. and Jaeger, J.C., Conduction of Heat in Solids, 2nd Ed., Oxford University Press (1959).

[15] Parker, W.J., "Development of a Model for the Heat Release Rate of Wood - A Status Report", NBSIR 85-3163, U.S. Dept. of Commerce, National Bureau of Standards (1985).

[16] Babraskas, V. and Krasny, J., "Predictions of Upholstered Chair Heat Release Rates from Bench-Scale Measurements", Fire Safety Sci. Eng. ASTM SP-882, Harmathy, T.Z., Ed., American Society for Testing and Materials, Philadelphia, 1985, pp.268-284.

[17] Kanury, A.M. and Martin, B.M., "A Profile of the Heat-Release Rate Calorimeter", International Symposium on Fire Safety of Combustible Materials, University of Edinburgh, UK (1975).

[18] Proposed Test Method for "Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter", P 190, American Society for Testing and Materials, Philadelphia, Pa.

[19] Kanury, A.M., "Modeling of Pool Fires with a Variety of Polymers", Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA (1975).

[20] Tewarson, A. and Pion, R.F., "Flammability of Plastics - I. Burning Intensity", Combustion and Flame, 26, 85-103 (1976).

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TABLE 1

Composite Materials

	Material	Resin Classification	Fiber Reinforcement	Potential Applications	Source
1.	Koppers Dion Panels	Polyester, Brominated	Glass Woven Roving	Boat Hull	Koppers Co., Inc.
2.	Derakane	Vinyl Ester type Epoxy	Glass	Pump Body, Duct Material, Bulkhead	Dow Chemical Co.
3.	Corflex Panel Assembly	Epoxy filled with aluminum silicate	Glass	Ventilation Ducts	Corflex Corp. per DTRC
4.	Ryton Panels	Poly(phenylene sulfide)	Glass: 1.Chopped Mat 2.Swirl Mat Prepreg 3.Woven Mat Prepreg Carbon(Graphite) Woven Prepreg	Undefined	Phillips Petroleum Co.
5.	Experimental 2-Ply Composite	Vinyl Poly(styryl pyridine)/Bismaleimide	Glass	Barrier material	Dow Chemical Co.
6.	Lab. Epoxy Panels	Epoxy	Graphite	Experimental	DTRC
7.	Lab. BMI Panels	BMI	Graphite	Experimental	DTRC

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TABLE 2

Ignition Delay Times for Composite Materials
Exposed to Various External Flux Levels

Ignition Delay Time (s)

Material (thickness)	Incident Flux (kW/m^2)			
	25	35	50	75
Koppers 6692T (25 mm)	263	120(10)*	60(2)	21
Dow Derakane (3 mm)	---	129	55	45(2)
Dow Derakane (25 mm)	---	390	187	55(2)
Corflex Panel (3 mm)	---	92(5)	54(2)	25
Corflex Assembly (37 mm)	---	122	70(0)	30(2)
Ryton Panels (3 mm):				
Glass Mat (Chopped)	---	183[+]	66	27(2)
Glass Mat Swirl	---	191(7)	97	28(5)
Glass Woven Mat Prepreg	---	154(7)	75	29(1)
Carbon Fiber: Woven Prepreg	---	N.I.	88	38(3)
Lab. Epoxy Panel (3 mm)[a]	---	116	76	40
Lab. BMI Panels (3 mm)[a]	---	211	126	54

*Numbers in parentheses indicate range about a mean where duplicate measurements were made.

[+]Duplicate tests performed; only one specimen ignited.

N.I. = No ignition during a 600 s exposure.

[a] Values taken from reference [13].

TABLE 3

Ignition Temperature of Six Polymers as
Measured by Thomason and Drysdale*

Material	Temperature (°C)
Polyoxymethylene	277 - 300
Poly(methyl methacrylate)-1[a]	298 - 328
Poly(methyl methacrylate)-2[a]	276 - 317
Polypropylene	331 - 345
Polystyrene	337 - 369
Polyethylene	360 - 367

a: Poly(methyl methacrylate)s from two different sources were used.

*Taken from Reference [12].

TABLE 4

Surface Temperature of Coated and Uncoated Graphite Fiber
Reinforced Composites 3 mm Thick at Pilot Ignition*

Resin/Coating	Incident Flux (kW/m^2)	Surface Temperature (°C)
Epoxy	35	390
	50	425
	75	375
Epoxy/Nextel Prepreg.	35	390
	50	400
	75	400
Bismaleimide	35	515
	50	500
	75	455
Bismaleimide/Nextel Prepreg.	35	455
	50	475
	75	440
Bismaleimide/Nextel Dry	35	455
	50	470
	75	490

*Taken from Reference [12]

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TABLE 5

Minimum External Flux for Long Exposure Time and for 300 s
Exposure To Cause Ignition Computed from the Regression of Ignition
Delay Time and External Flux

Material	Regression Slope	$MERF_{600}$ [a] (kW/m^2)	$MERF_{300}$ [b] (kW/m^2)
Koppers 6692T (25 mm)	-2.3	18	24
Derakane Panel (3 mm)	-1.5	13	20
Derakane Panel (25 mm)	-2.7	31	40
Corflex Panel (3 mm)	-1.7	12	18
Corflex Assembly	-1.9	15	22
Ryton Panels (3.2 mm):			
Glass Mat (Chopped)	-2.5	21	28
Glass Mat (Swirl)	-2.6	23	31
Glass Woven Mat Prepreg	-2.1	18	25
Carbon Woven Prepreg	-2.1	20	28

a: Minimum External Radiant Flux necessary to cause ignition after 600
     second exposure.
b: Minimum External Radiant Flux necessary to cause ignition after a 300
     second exposure.

TABLE 6

Results of Averaging the Rate of Heat Release of 25 mm (1 in)
Koppers Dion 6692T Panels (FR Polyester/Glass Fiber Composite)

Experiment Number	Flux (kW/m²)	Average Rate of Heat Release (kW/m²)					
		60 s	120 s	180 s	240 s	300 s	360 s
1094	25	50	40(35)*	35(25)	30(5)	25(5)	20(<5)
1095	35	55	65(60)	55(40)	70(35)	65(25)	60(20)
1096	35	70	55	45	40	40	35(25)
1086	50	60	50(40)	45(35)	45(35)	40(35)	40(35)
1087	50	60	45(35)	40(25)	35(25)	35(25)	30(25)
1097	75	80	80(75)	70(55)	65(40)	60(40)	55(40)

*Values in parentheses are averaged over the previous 60 sec interval.

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TABLE 7

Influence of Glass Fiber Configuration on the Ignition Delay
and Average Rates of Heat Release of Koppers Dion Polyester Composites Irradiated
at 50 kw/m²

Resin	Fiber Reinforcement	t_{ig} (s)	$\dot{q}''(t)$, kW/m²					
			60 s	120 s	180 s	240 s	300 s	360 s
1. Iso-orthophthalic Polyester, 42%	Glass Combo	55	215	180 (145)*	165 (135)	155 (125)	150 (118)	145 (125)
2. Isophthalic (unsaturated), 43% Polyester, 51%	BI PLY	50	210	75 (145)	65 (135)	155 (130)	145 (120)	145 (120)
3. Isophthalic (unsaturated) Polyester, 43%	Glass Combo	45	235	190 (150)	175 (140)	165 (135)	160 (130)	155 (130)
4. Brominated Iso-phthalic Polyester, 54%	Glass Woro Mat	35	135	115 (95)	105 (85)	100 (85)	100 (85)	95 (85)
5. Brominated Iso-phthalic Polyester, 42%	Woro S2	45	130	110 (90)	100 (80)	95 (80)	0 (80)	0 (80)

Fiber Reinforcement:
  Glass Combo = stitched woven roving and chopped strand
  BI PLY = woven roving and woven mat
  Glass Woro Mat = non woven spirally interlocked fibers
  Glass Woro S2 = same as woro mat of S2 glass
* Values in parentheses are interval (60 s) arranged

TABLE 8

Interval Averaged Rate of Heat Release of 3 mm Corflex Panels and Panel Assembly
(FR Epoxy-Fiberglass Composites)

Experiment Number	Sample	Flux, kW/m²	60 s	120 s	180 s	240 s	300 s	360 s
1137	Corflex Panel	35	170	155 (140)*	160 (175)	140 (7)	- -	- -
1170	Corflex Panel	35	170	170 (170)	160 (145)	130 (30)	105 (15)	90 (10)
1534	Corflex Panel	50	175	190 (205)	155 (90)	120 (20)	100 (10)	- -
1535	Corflex Panel	50	175	180 (185)	180 (180)	145 (45)	120 (20)	105
1161	Corflex Panel	75	215	215 (215)	165 (75)	130 (25)	- -	- -
1140	Corflex Assembly	35	170	145 (120)	135 (115)	120 (80)	105 (50)	95 (30)
1536	Corflex Assembly	50	160	145 (135)	145 (145)	135 (100)	120 (60)	105 (40)
1537	Corflex Assembly	50	170	155 (140)	150 (140)	135 (95)	120 (55)	105 (35)
1155	Corflex Assembly	75	190	185 (180)	170 (140)	145 (75)	125 (50)	- -
1154	Corflex Assembly	75	190	185 (175)	160 (115)	135 (65)	115 (40)	100 (30)

*Values in parentheses are averaged over the previous 60 s interval.

TABLE 9

Interval Averaged Rates of Heat Release of 25 mm Thick Dow Derakane Pump
Housing (Vinyl Ester Epoxy-Fiber Glass Composite)

Experiment Number	Flux, kW/m²	Average Rate of Heat Release (kW/m²)					
		60 s	120 s	180 s	240 s	300 s	360 s
1172	35	295	255 (110)*	220 (130)	200 (111)	180 (111)	165 (100)
1550	50	225	195 (160)	170 (130)	155 (115)	145 (105)	140 (100)
1084	50	190	170 (150)	160 (145)	160 (150)	160 (160)	160 (155)
1150	75	240	225 (205)	210 (175)	195 (160)	185 (140)	175 (125)
1151	75	217	205 (190)	190 (160)	175 (140)	165 (130)	160 (140)
1158	75	240	225 (205)	215 (190)	200 (150)	185 (135)	175 (125)

*Values in parentheses are averaged from the previous 60 s interval.

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TABLE 10

Interval Averaged Rates of Heat Release of 3 mm
Thick Laboratory Samples of Epoxy-Graphite Fiber
Composite Panels[a]

		Average Rate of Heat Release (kW/m^2)					
Experiment Number	Flux (kW/m^2)	(60 s)	(120 s)	(180 s)	(240 s)	(300 s)	(360 s)
	35	150	155 (160)*	120 (50)	95 (20)	75 (≈0)	
2302	50	185	170 (155)	135 (60)	105 (15)	85 (10)	75 (10)
2311	75	210	190 (165)	145 (60)	150 (25)	100 (≈0)	

(a) Taken from Ref. [12]
* Values in parentheses are averaged over the previous 60 s interval.

TABLE 11

Results of Post-Ignition Averaging of the Rate of Heat
Release of 3 mm Thick Ryton Panels (Reinforced Poly(phenylene sulfide))

Experiment Number	Fiber Reinforcement	Flux (kW/m²)	Average Rate of Heat Release (kW/m²)					
			60 s	120 s	180 s	240 s	300 s	360 s
1385	Chopped Mat	35	50	30 (10)*	20 (5)	20 (10)	20 (20)	20 (25)
1386			N.I.	- -	- -	- -	- -	- -
1545		50	75	65 (60)	70 (75)	85 (135)	90 (105)	80 (30)
1374		75	110	115	130	130	115	100
1381		75	100	95 (95)	105 (125)	120 (155)	110 (75)	100 (45)
1387	Swirl Mat	35	20	10 (5)	10 (5)	10 (5)	10 (10)	10 (15)
1388		35	<5	≈0 (0)	≈0 (0)	0 (0)	0 (0)	0 (0)
1543		50	35	45 (55)	50 (65)	55 (60)	55 (60)	55 (55)
1375		75	75	110 (140)	115 (135)	135 (180)	135 (150)	120 (40)
1382		75	90	110 (130)	110 (115)	130 (180)	120 (100)	105 (30)

TABLE 11 (Continued)

Experiment Number	Fiber Reinforcement	Flux (kW/m²)	Average Rate of Heat Release (kW/m²)					
			60 s	120 s	180 s	240 s	300 s	360 s
1389	Woven Mat	35	10	5	<5	<5	<5	<5
1390		35	5	5	<5	<5	<5	<5
1544		50	35	45 (60)	50 (64)	55 (95)	55 (110)	55 (45)
1379		75	85	90	95	100	95	80
1383		75	80	85 (85)	90 (110)	95 (110)	90 (60)	80 (25)
1391	Woven Mat	35	N.I.	--	--	--	--	--
1392	Graphite Fibers	35	N.I.	--	--	--	--	--
1546		50	60	90 (115)	115 (60)	95 (35)	80 (20)	70 (25)
1380		75	85	120 (150)	120 (130)	100 (40)	90 (35)	80 (35)
1384		75	100	130	125	105	90	80

N.I. = No Ignition

*Values in parentheses are averaged over the previous 60 s interval

TABLE 12

Results of Post-Ignition Averaging of the Rate of Heat
Release of a 3 mm Thick Laboratory Sample of
BMI-Graphite Fibers Composite[a]

Experiment Number	Flux (kW/m²)	Average $\dot{q}''$ (kW/m²)					
		(60 s)	(120 s)	(180 s)	(240 s)	(300 s)	(360 s)
2296	35	105	130	135	120	105	90
			(130)*	(140)	(90)	(40)	(10)
2308	50	120	145	145	130	110	96
			(170)	(150)	(90)	(35)	(15)
2313	75	140	170	165	145	125	105
			(200)	(155)	(75)	(30)	(25)

(a) Taken from Reference [12]
* Values in parentheses are averaged from the previous 60 s interval.

TABLE 13

Results of Post-Ignition Averaging of the Rate of Heat
Release of a 2-Ply-Reinforced Vinyl Poly(styryl pyridine) - BMI
Resin Experimental Composite

Experiment Number	Flux, kW/m²	Average q̇", kW/m²					
		60 s	120 s	180 s	240 s	300 s	360 s
1168	35	10	5(<5)*	5(≈0)	<5(≈0)	<5(≈0)	- -
1146	35	7	5(<5)	5(<5)	- -	- -	- -
1548	50	25	19(15)	16(10)	15(10)	15(15)	15(15)

* Values in parentheses are averaged from the previous 60 s interval.

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TABLE 14

Comparison of Inferred Flammability Indices of Composite Materials

	$\Delta H_{c,eff}$ (kW/m²)	TSI*	ESI+ (kW/m²)	MERF$_{30g}$ (kW/m²)
Koppers Dion 6692T (25 mm)	12 ± 2	0.6	30	24
Corflex Panel (3 mm)	12 ± 0.9	1.1	125	18
Corflex Panel Assembly (37 mm)	12 ± 0.4	0.6	100	22
Lab. Epoxy Panel (3 mm)	20	1.4	100	18
Lab. BMI Panel (3 mm)	20	0.9	75	28
Ryton Panels (3 mm)				
Chopped Mat	25 ± 1.6	1.3	5	28
Swirl Mat	22 ± 2.0	1.6	-55	31
Woven Mat	23 ± 2.2	1.8	-40	25
Graphite Woven Mat	23 ± 0.03	1.6	--	28
Average	23 ± 1.3	1.6 ± .20		28 ± 2.4

* TSI = Thermal sensitivity index.
+ ESI = Extinction sensitivity index.

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TABLE 15

Average Yields of Combustion Products for Various Types of Composite Materials

	Flux (kW/m²)	Initial Mass, g	Total Wt Loss, %	Extinction Areas (m²/kg)	Hydrocarbons[a]	CO[a]	CO₂[a]
Koppers Dion							
6692T	25	465	6	1630	0.10	0.008	0.09
1095	35	471	9	1500	0.10	0.010	0.11
1096	35	471	11	970	0.07	0.011	0.16
1086	50	467	17	1205	0.06	0.011	0.11
1097	75	466	20	1570	0.03	0.012	0.17
Corflex Panel							
1137	35	60	56	2600	0.09	0.011	0.77
1170	35	54	52	2600	0.08	0.015	0.87
1534	50	54	54	1835	0.08	0.132	2.63
1535	50	63	56	1790	0.01	0.014	0.78
1161	75	55	56	2805	≈0	0.013	0.77
Lab. Epoxy Panels							
	35	69	17	740	0.02	0.04	1.9
	50	74	20	790	0.02	0.10	0.9
	75	73	19	800	0.01	0.06	1.4
Lab. BMI Panels							
	35	74	24	530	0.02	0.04	1.6
	50	76	24	600	0.02	0.04	1.5
	75	76	26	760	0.01	0.02	1.5
Ryton Panels (Swirl Mat)							
1385	35	54	23	270	0.05	0.38	0.93
1545	50	54	24	630	0.009	0.15	1.42
1381	75	56	32	490	0.004	0.14	1.50

(a) Ratio average of mass generation rate to the mass loss rate

Table 16

Ratio of Average Yields for CO/CO_2, HC/CO_2, and σ/CO_2 for Various Types of Composite Materials at Different External Irradiances

Materials	Flux (kW/m²)	CO/CO_2	HC/CO^2	σ/CO_2 (m²/kg) (x10⁻⁴)
Koppers				
6692T	25	0.09	1.11	1.8
1095	35	0.09	0.91	1.3
1096	35	0.07	0.44	0.6
1086	50	0.10	0.55	1.1
1097	75	0.07	0.18	0.9
Corflex Panels				
1137	35	0.01	0.12	0.3
1170	35	0.02	0.09	0.3
1534	50	0.05	0.03	0.1
1535	50	0.02	0.01	0.2
1161	75	0.02	--	0.4
Lab. Epoxy/ Graphite	35	0.02	<0.01	0.04
	50	0.11	0.02	0.09
	75	0.04	<0.01	0.06
Lab. BMI/ Graphite	35	0.03	0.01	0.03
	50	0.03	0.01	0.04
	75	0.01	0.01	0.05
PPS/Chopped Mat				
1385	35	0.33	0.05	0.03
1545	50	0.11	0.01	0.04
1381	75	0.09	<0.01	0.03

Laser extinction beam

Temperature and differential pressure measurements taken here

Soot sample tube location

Exhaust blower

Exhaust hood

Gas samples taken here

Cone heater

Soot collection filter

Spark igniter

Sample

Controlled flow rate

Load cell

Vertical orientation
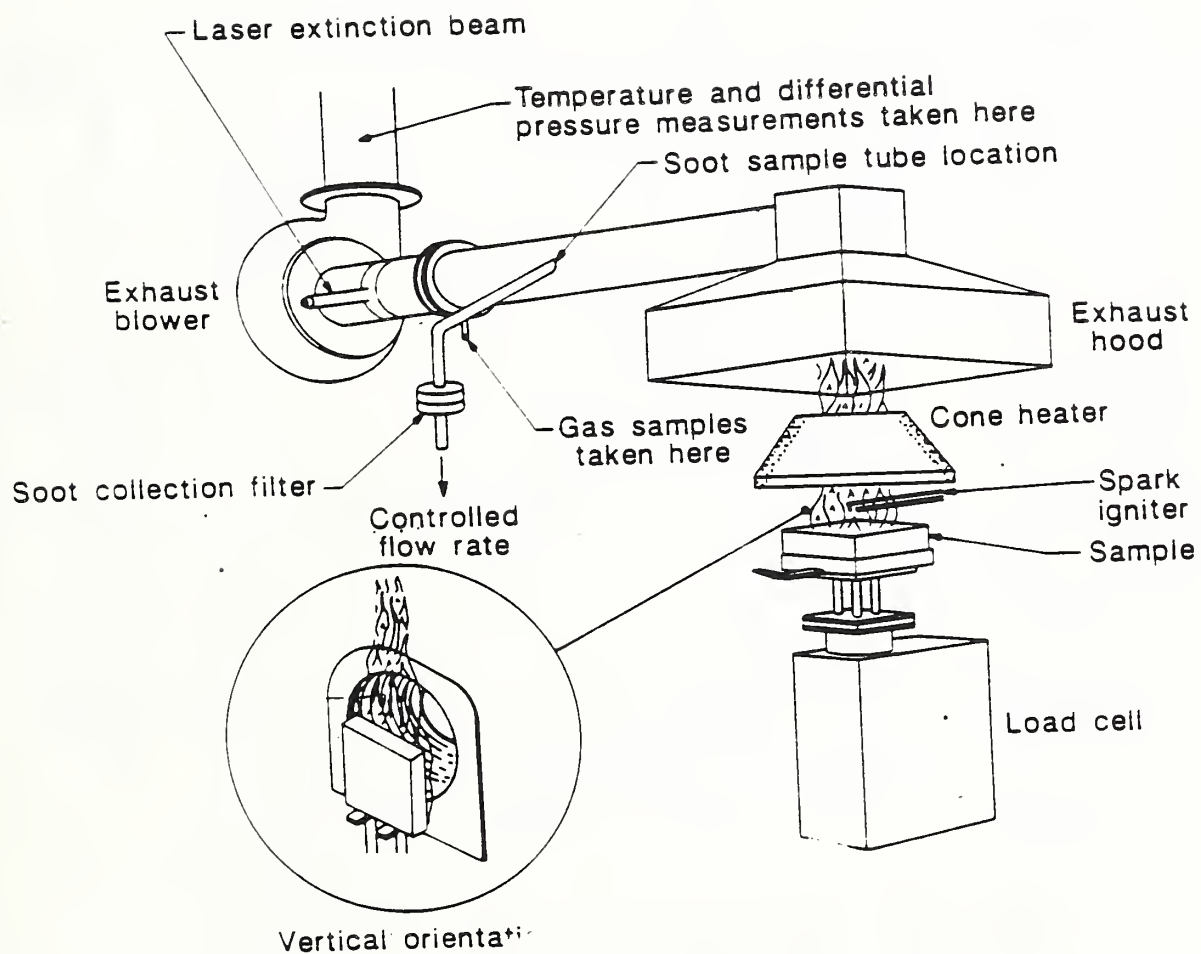
Figure 1.   Schematic Representation of Cone Calorimeter

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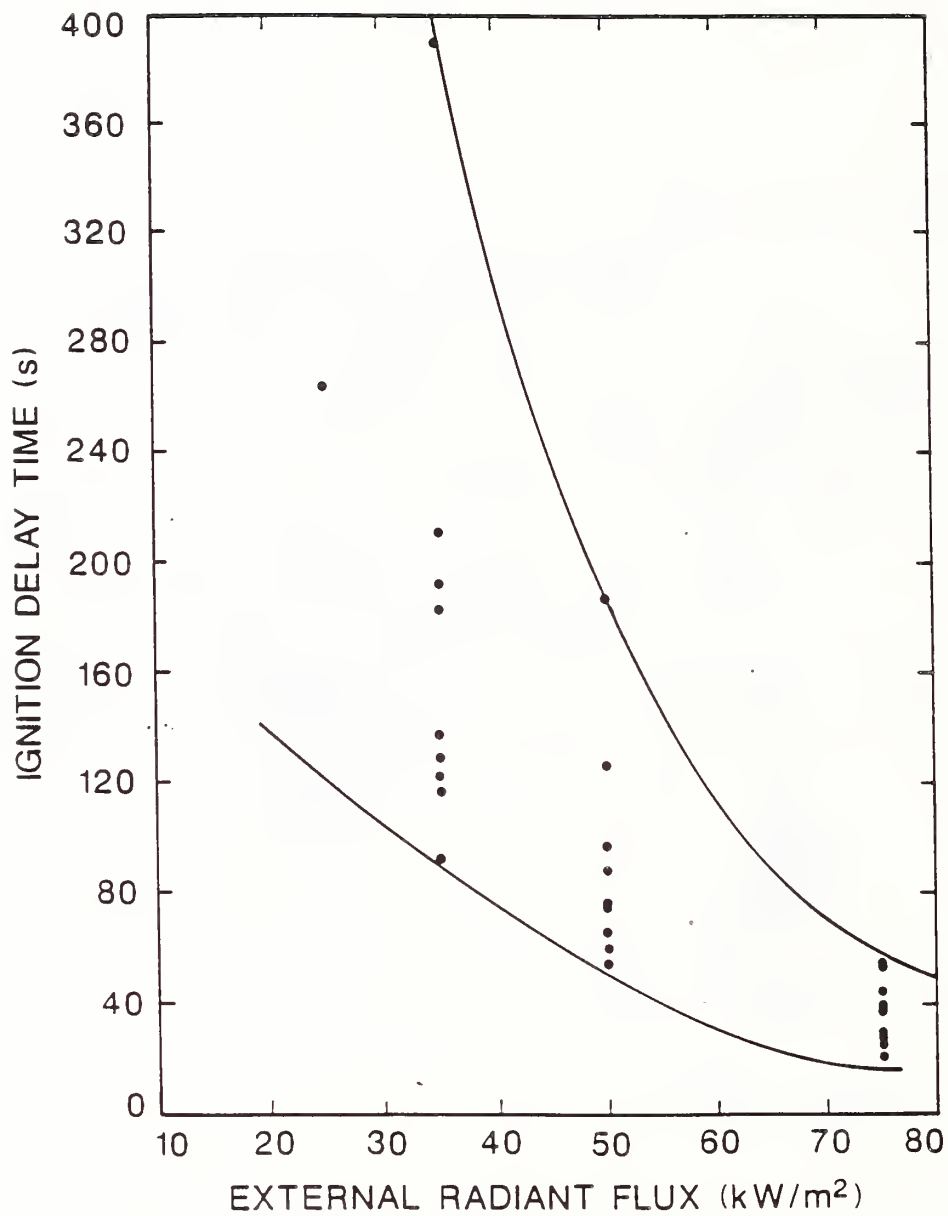
Figure 2.   Range of Ignition Delay Times as a Function of External
Radiant Flux for All Composites
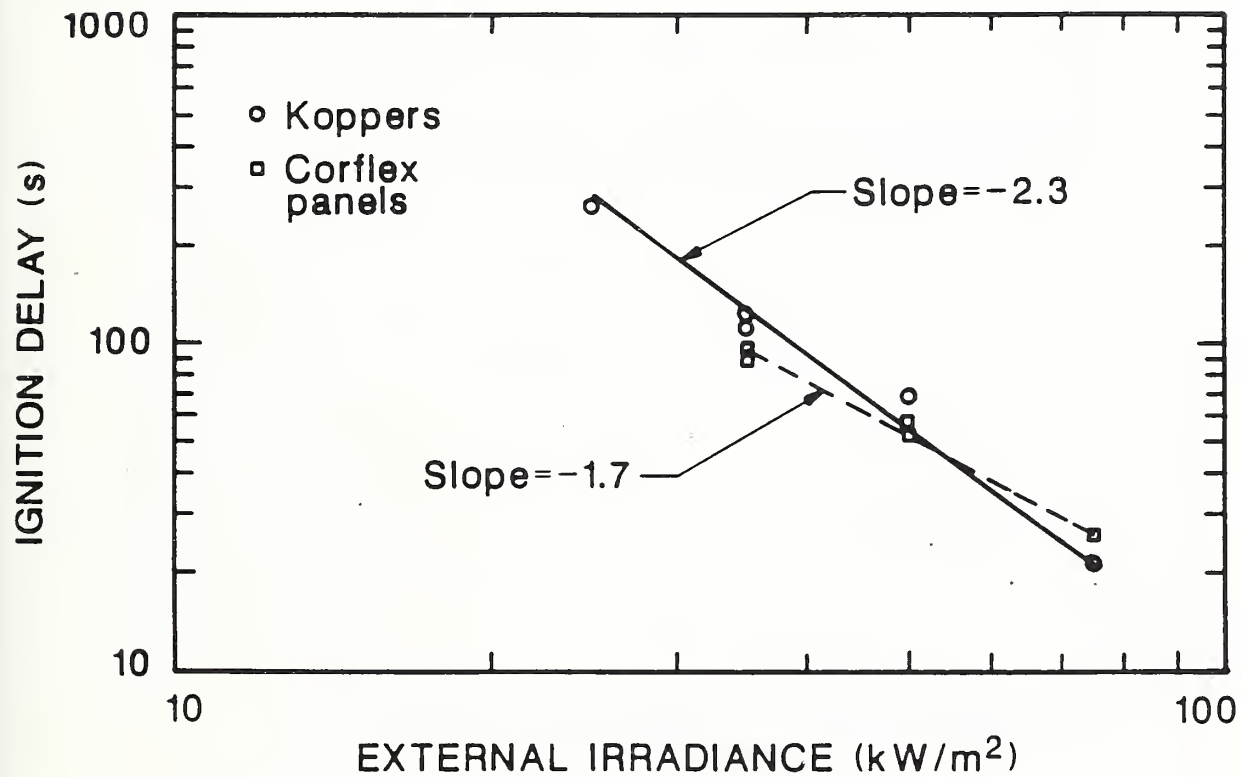
Figure 3.   Ignition-Delay Time for Two Composites as a Function of
External Radiant Flux
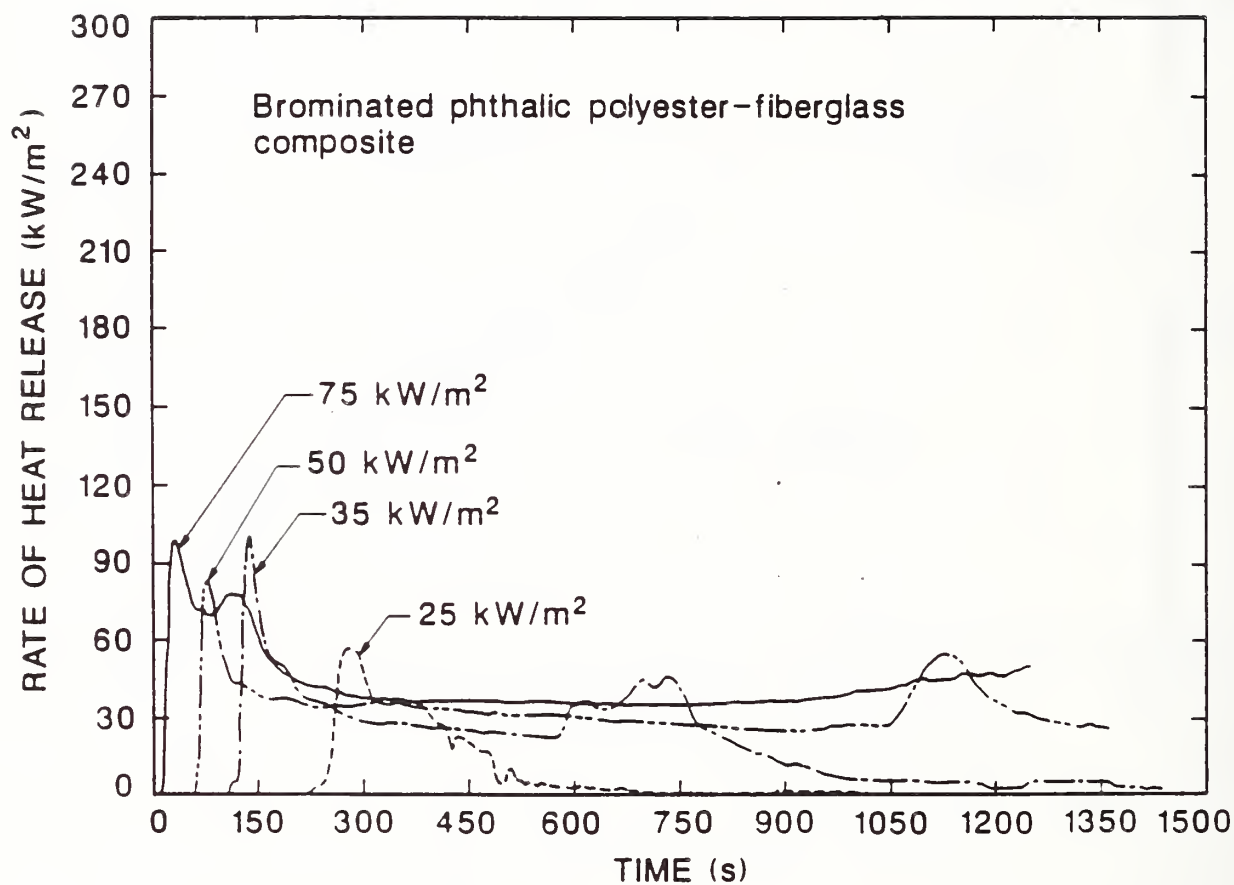
Figure 4. Effect of Irradiance on the Rate of Heat Release from a
25 mm FR Polyester/Glass Composite
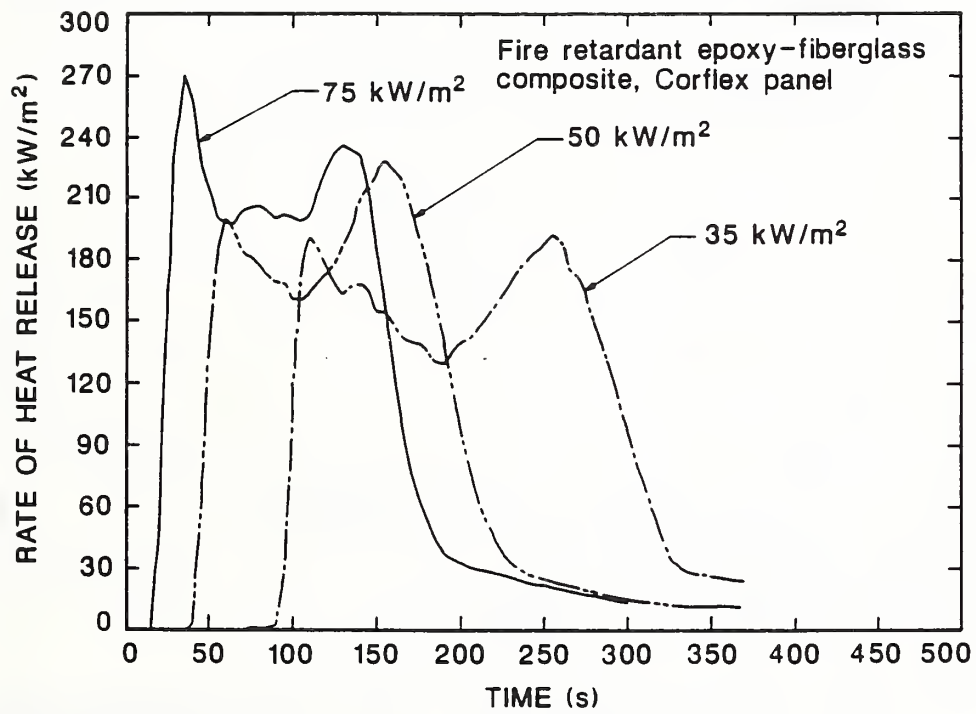
Figure 5.   Effect of Irradiance on the Rate of Heat Release from a
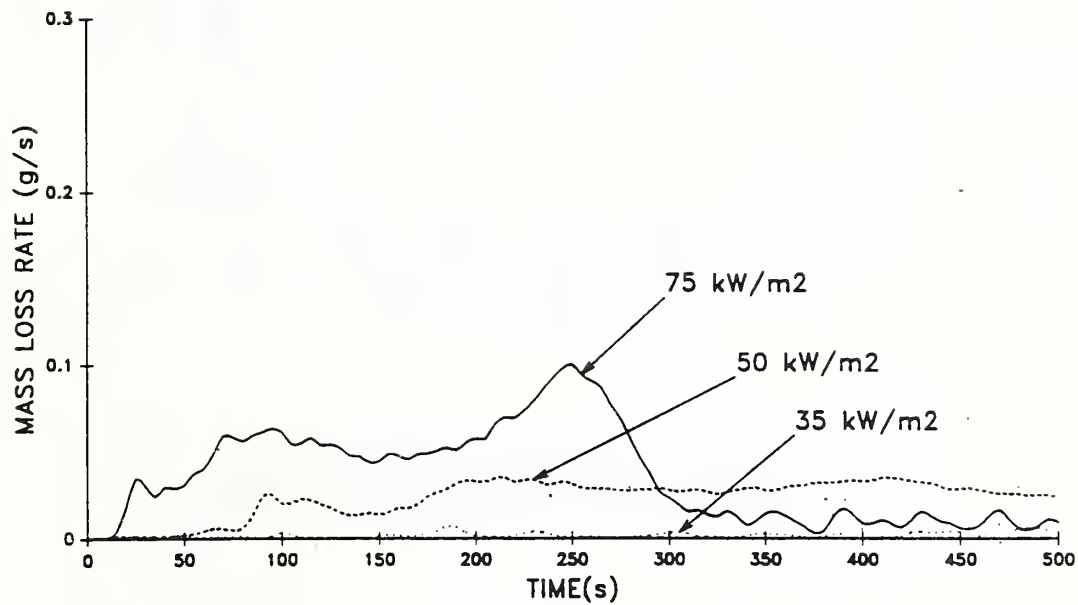3 mm FR Epoxy/Fiber Glass Composite

51
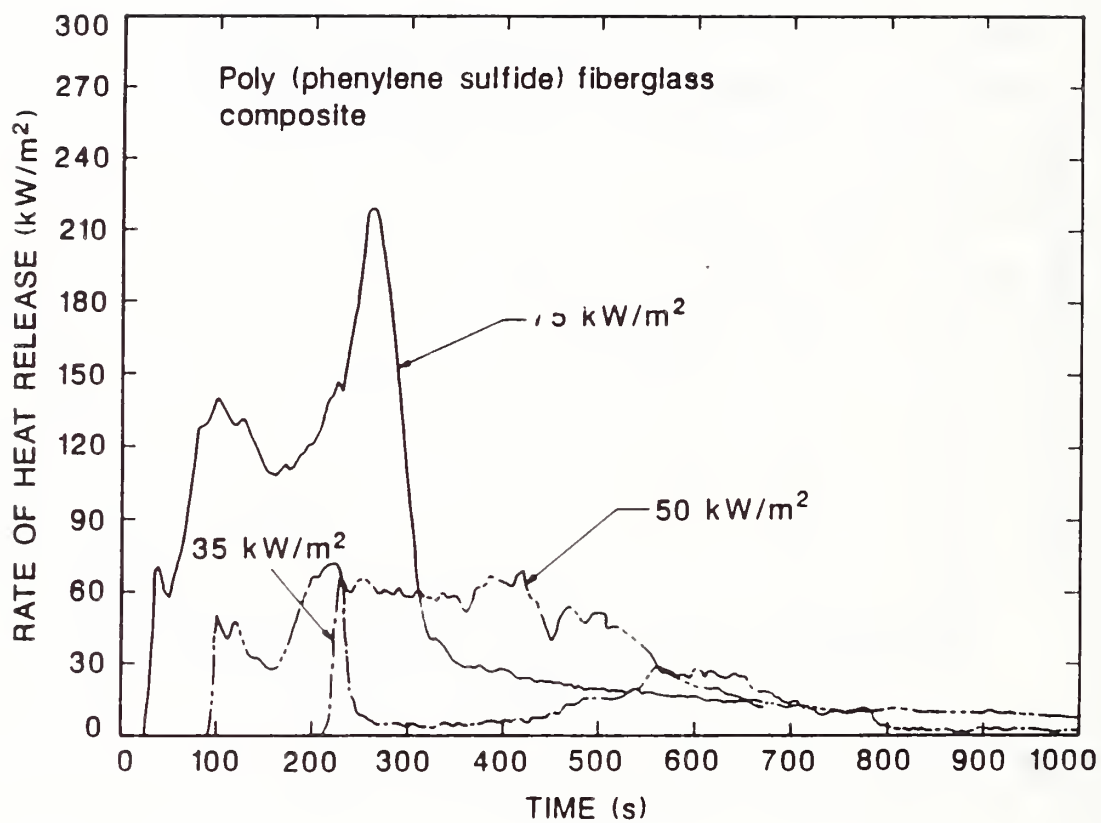
Figure 6.   Effect of Irradiance of the Rate of Heat Release from
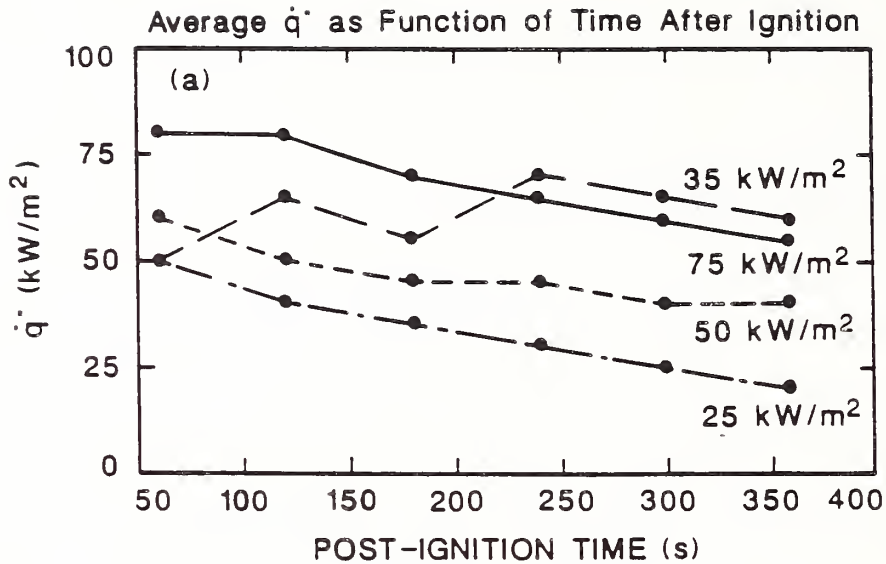from 3 mm Poly(phenylene Sulfide)/Fiber Glass Composite

52
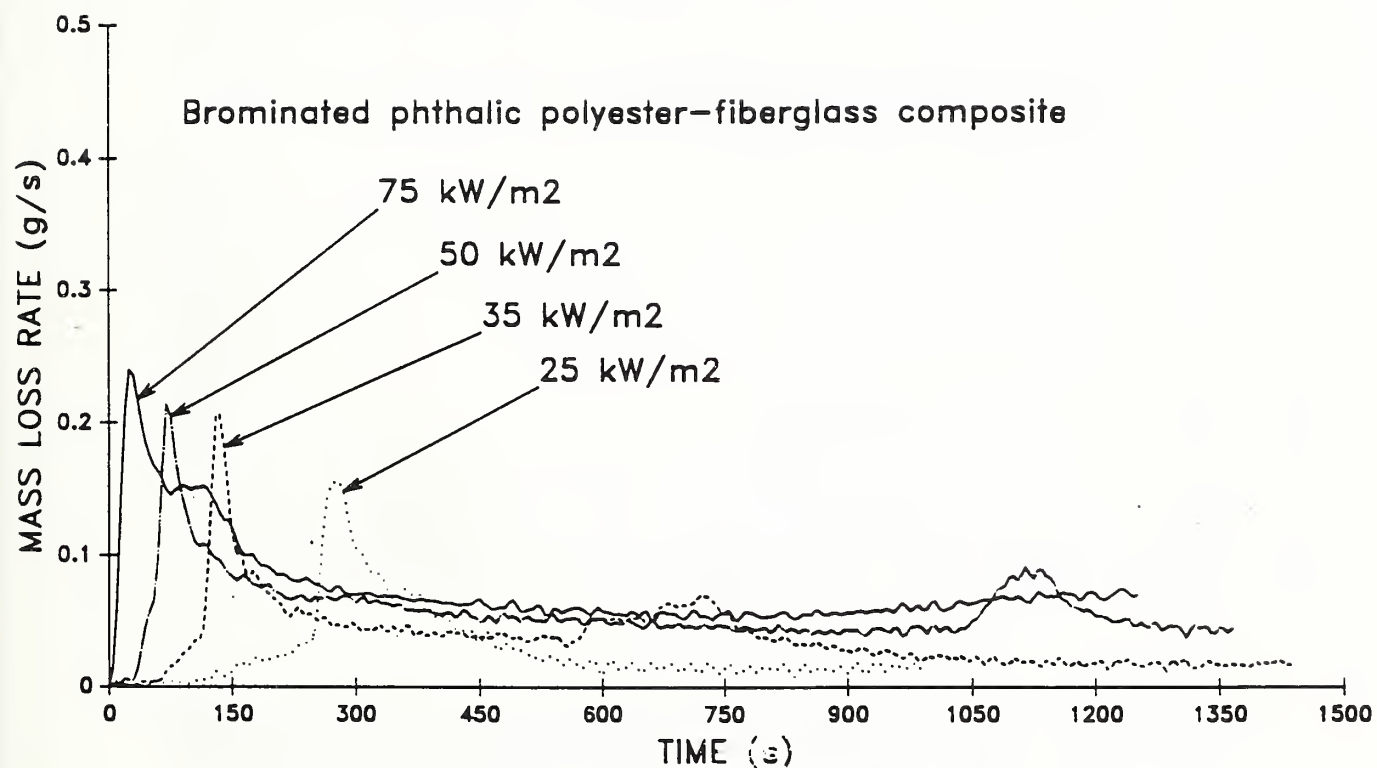
Figure 7. Effect of Irradiance on the Mass Loss Rate from a FR Polyester/
Fiber Glass Composite
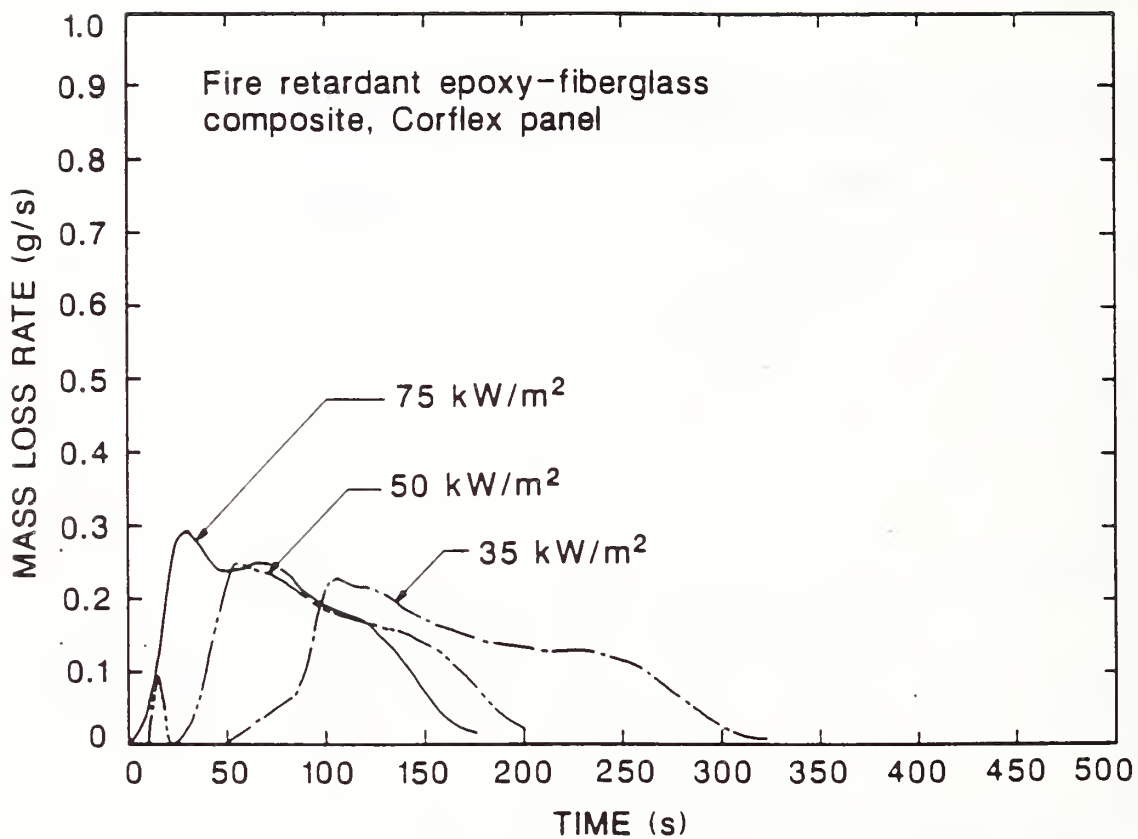
Figure 8.   Effect of Irradiance on the Mass Loss Rate from a 3 mm Thick
FR Epoxy/Fiber Glass Composite

Figure 9. Effect of Irradiance on the Mass Loss Rate from a 3 mm Thick Poly(phenylene Sulfide)/Fiber Glass Composite

Average $\dot{q}$ as Function of Time After Ignition

(a)

$\dot{q}$ (kW/m^2)

POST-IGNITION TIME (s)

35 kW/m^2
75 kW/m^2
50 kW/m^2
25 kW/m^2

Interval (60s) Averaged $\dot{q}$ After Ignition

(b)

$\dot{q}$(kW/m^2)

POST-IGNITION TIME (s)

75 kW/m^2
50 kW/m^2
25 kW/m^2
35 kW/m^2
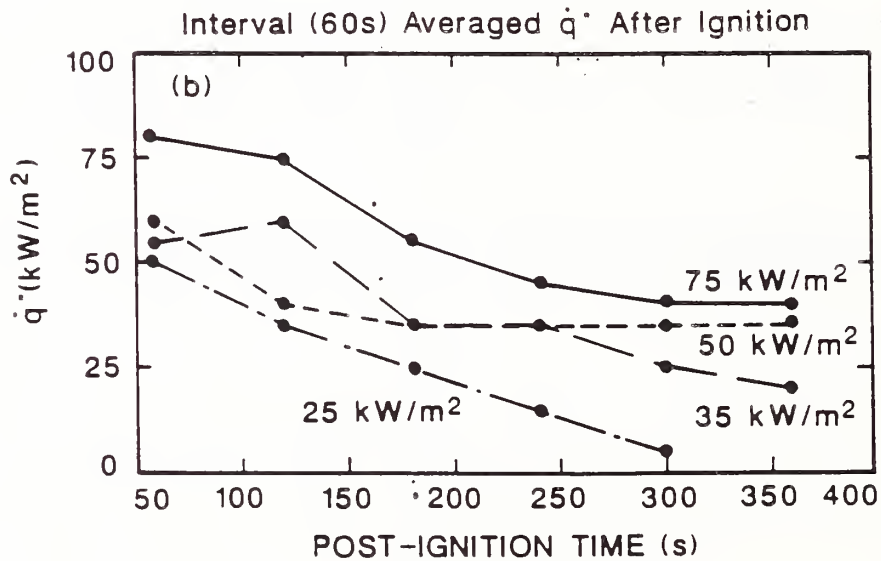
Figure 10. Average $\dot{q}$ as a Function Time After Ignition of Irradiatively
Heated Koppers Dion 6692T Composite (FR Polyester/Glass)
Panels
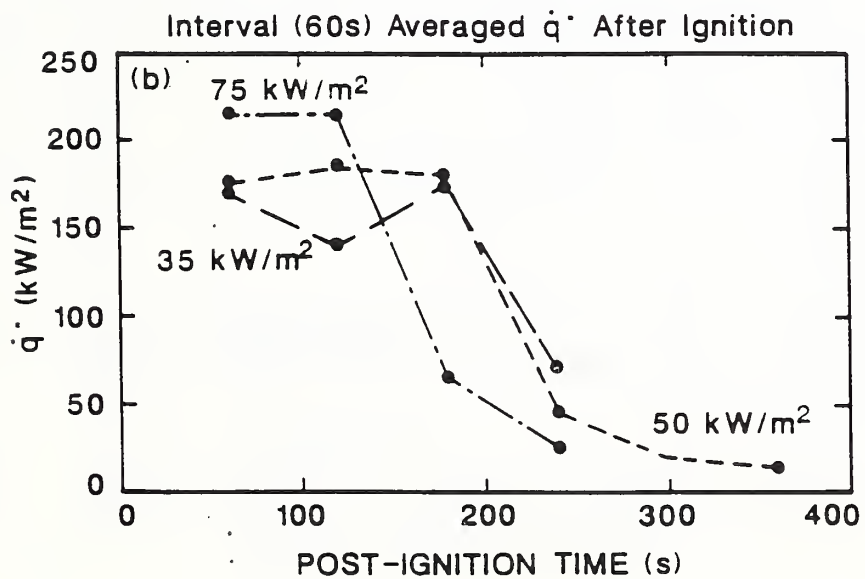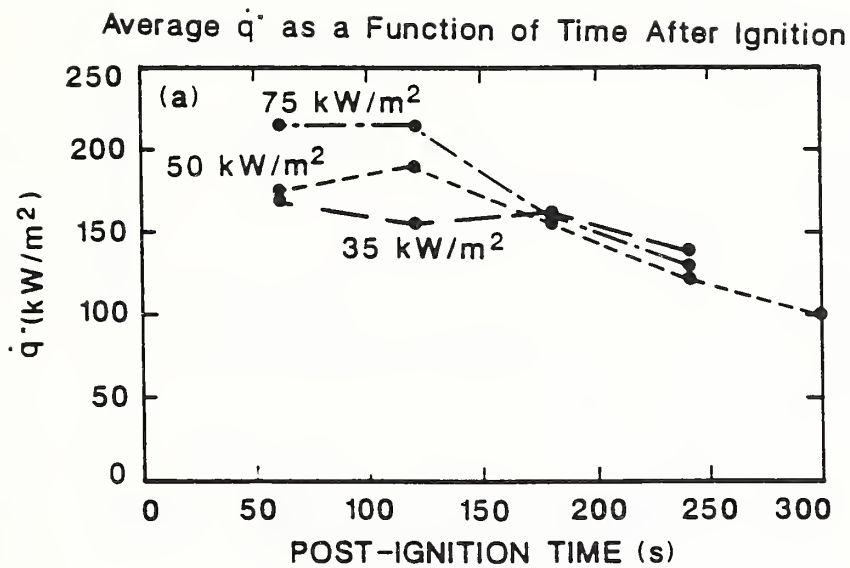
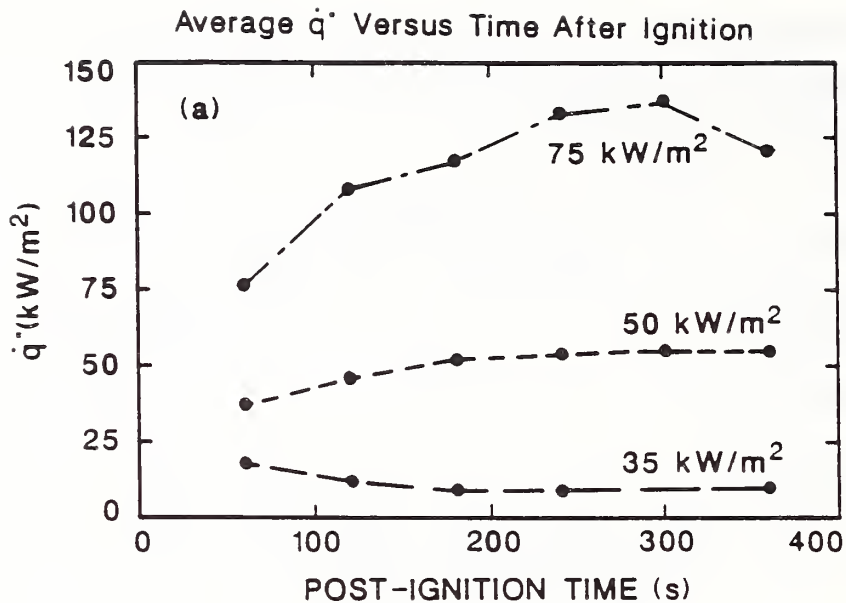Figure 11. Average q̇ as a Function of Time After Ignition of Irradiativel Heated 3 mm Corflex (FR Epoxy/Glass) Panels
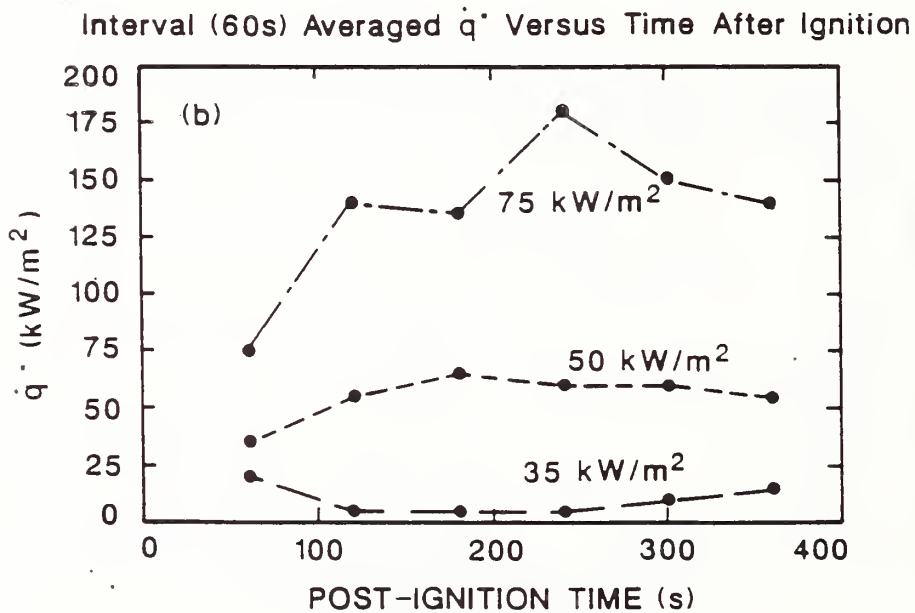
Figure 12. Average q̇ as Function of Time After Ignition for
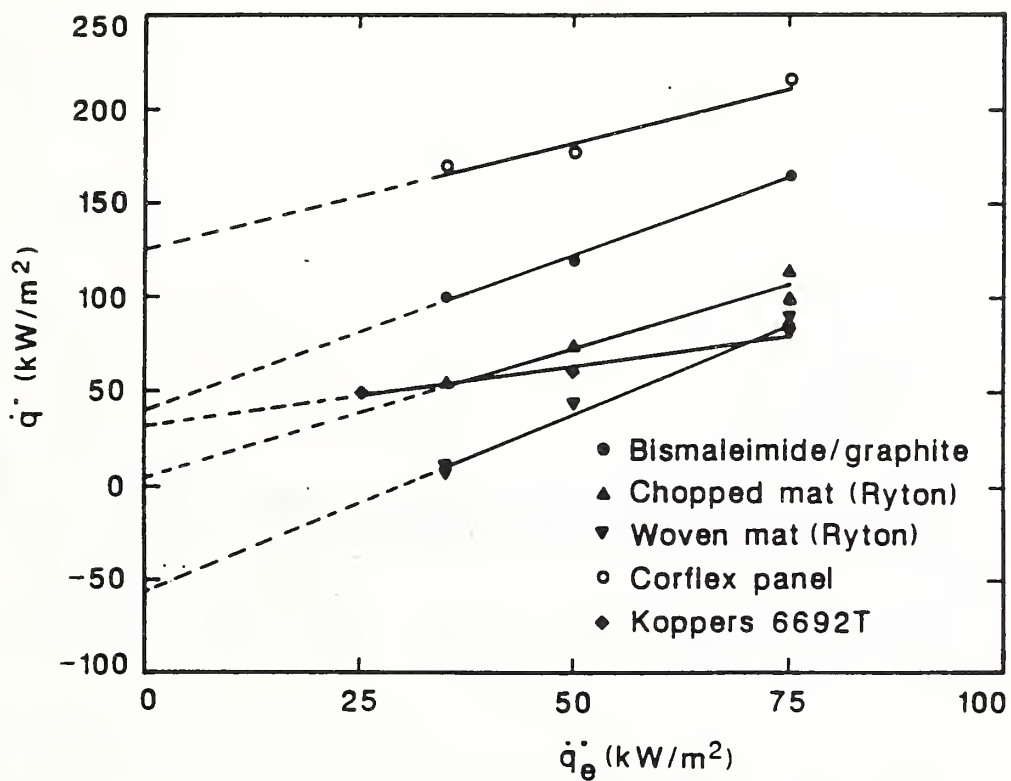Irradiatively Heated 3 mm Ryton Panels (Poly(phenylene
sulfide)/Fiber Glass)

Figure 13. Average Rate of Heat Release Up to 60 s Post Ignition of Several Composites as a Function of External Flux
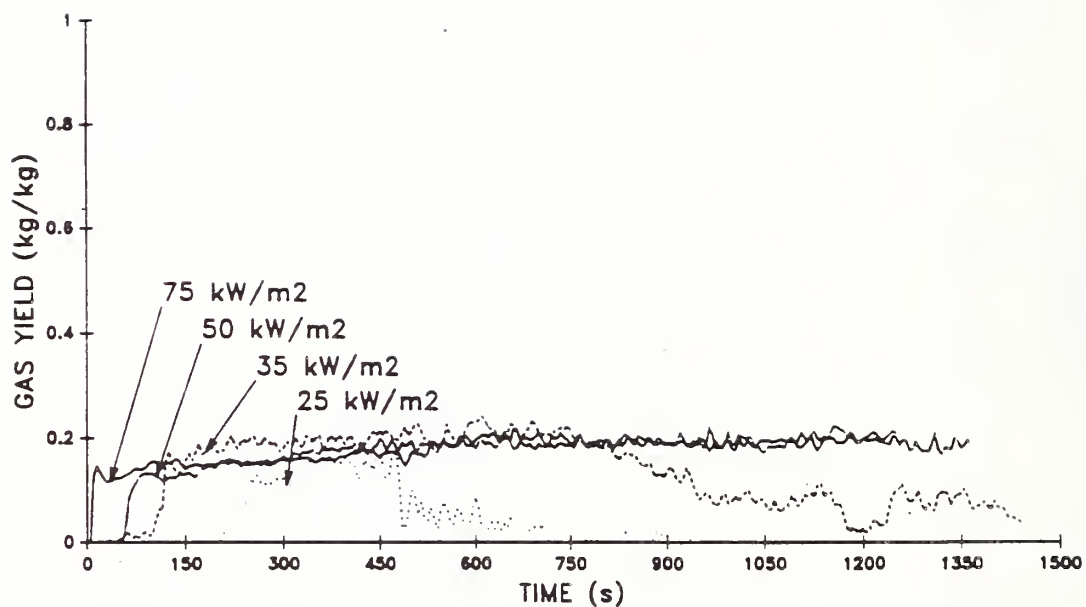
Figure 14. The Effect of Irradiance on the Production of CO_2 from 25 mm FR Polyester-Fiber Glass Composite
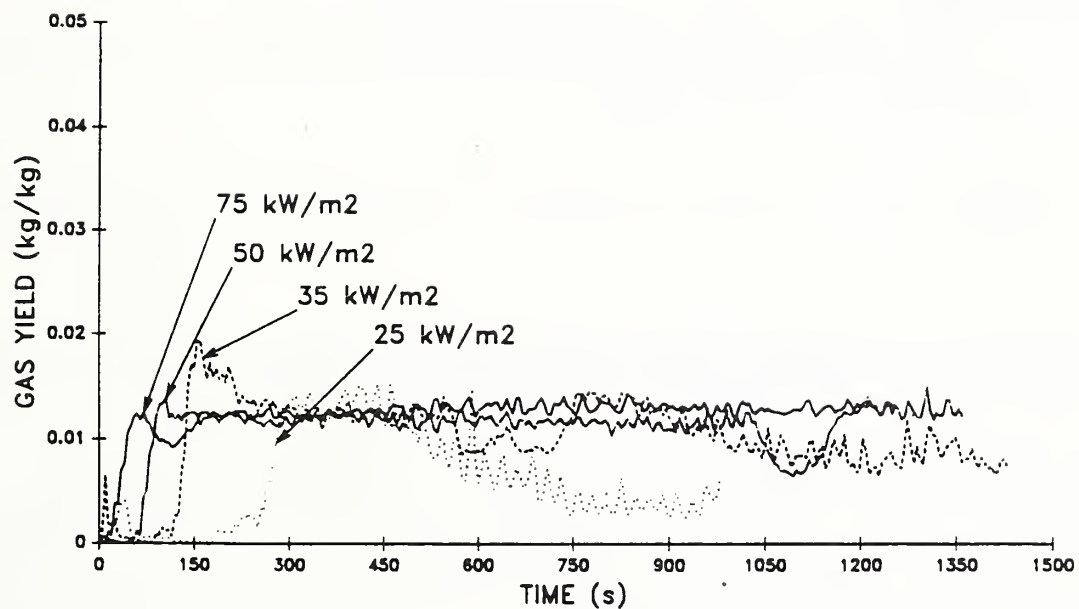
Figure 15. The Effect of Irradiance on the Production of CO from a
FR Polyester/Fiber Glass Composite

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

A study was undertaken to evaluate the fire performance of composite materials using the cone calorimeter as the bench-scale method of test simulating the thermal irradiance from fires of various magnitudes. Five parameters were derived from the calorimetery measurements to characterize the ignitability amd flammability of the composite materials. Three of the parameters are, to a large extent, empirical since radiative heat losses from the samples were unknown. These parameters are: 1) minimum external radiant flux (MERF) required to produce pilot ignition in a predetermined exposure time; 2) thermal sensitivity index (TSI) which indicates the burning intensity dependence on external heat flux; and 3) extinction sensitivity index (ESI) which indicates the propensity for continued flamming combustion without an external heat flux. MERF valves at 300 s for 3 mm composites panels of a FR epoxy resin and a poly(phenylene sulfide) (PPS) resin composites were about 18 and 28 kW/m^2, respectively. The TSI of the PPS resin composite had the greatest dependency on external flux. Additionally, the ESP of the PPS composites was the only one to indicate an external flux requirement to sustain combustion during the first 60 s after ignition. The other two parameters determined were yields of gaseous products of combustion and average extinction area, σ, normalized to the CO_2 yields.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

combustion; composite materials; cone calorimeters; extinction; fiberglass resins; flammability; heat release rate; ignition; resins; smoke; thermal decomposition

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